NRL Report 7273

An Evaluation of Nonlinear Optical Materials by the Second-Harmonic Powder Technique

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Central Materials Research Activity

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An important area of research in nonlinear optics is the development of new crystalline materials having suitable nonlinear optical properties. In nonlinear device applications, such as frequency conversion and generation, modulation, and control of optical beams, improvements in performance and in spectral range depend on improved properties of the nonlinear crystals employed.

There are several criteria to consider in determining a crystal's usefulness for nonlinear optical experiments: (a) acentric symmetry class, for nonvanishing second-order nonlinear susceptibility; (b) high transparency in the spectral region of interest; (c) sufficient birefringence to allow phase matching; (d) large nonlinear susceptibility coefficients; (e) good physical characteristics, such as surface hardness and insolubility; and (f) resistance to optical radiation damage.

A recent experimental technique developed by Kurtz and Perry [1,2], and independently studied by Graja [3], allows a rapid initial evaluation of the nonlinear optical properties of crystalline material in powdered form. The technique involves the measurement of laser-induced second-harmonic radiation produced from powdered samples of graded particle sizes. The measured harmonic intensity is then compared quantitatively against a reference material whose nonlinear optical properties are known. By this means a rapid determination can be made whether a material is acentric and whether it has relatively large nonlinear coefficients and is phase matchable. Hence materials that show little promise can be eliminated without requiring the time-consuming growth of single crystals of sufficient size and quality for evaluation.

At NRL a cooperative research program has been undertaken by the Central Materials Research Activity and the Quantum Optics Branch into the development and growth of nonlinear crystals for use in the visible and infrared spectral regions. This report describes the use of the second-harmonic powder technique at 1.06 μm to investigate several crystals, principally of the iodate family, for their potential as nonlinear materials.

THEORY

A detailed discussion of the theory of second-harmonic generation in crystalline powders is given in the original paper of Kurtz and Perry [1]. In this section we will sketch their analysis and indicate the basis for distinguishing between phase-matchable (PM) and non-phase-matchable (NPM) materials.

It is assumed that a powdered sample contains graded particles of average thickness $\hat{r}$, densely packed in a thin layer of thickness L, and that the diameter of the laser beam is $D >> \hat{r}$ so that a statistically large number of particles of random orientation are encountered. The analysis involves an angular average of the second-harmonic intensity $I^{2\omega}$ over terms involving the nonlinear tensor susceptibility $d^{2\omega}_{ijk}$ and the coherence length $\ell_c = \lambda/4(n_{2\omega} - n_\omega)$. For NPM materials an average value for coherence length may be taken, typically of the order 1 to 10 μm at visible wavelengths, and the angular average performed only over $d^{2\omega}_{ijk}$; however, for PM materials, in which $n_{2\omega} - n_\omega \to 0$ in certain crystal directions, the angular average must include the angular dependence of ℓ_c. A comparison

between the second-harmonic intensity $I^{2\omega}$ generated from NPM and PM materials and its dependence on average particle size $\hat{r}$ can be made as follows:

NPM case. For $\hat{r} < \ell_c$, $I^{2\omega}$ increases with particle size, reaching a maximum value at $\hat{r} \approx \ell_c$. $I^{2\omega}$ then decreases inversely with $\hat{r}$, since the second harmonic generated in each particle remains constant while the density of particles in the fixed volume decreases. Thus, for a NPM material in the limit of large $\hat{r}$ ($>>\ell_c$),

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$$I^{2\omega} \propto (d_{PM}^{2\omega})_{av}^2 \, [(\pi^2/4)\ell_c' \sin \theta_{PM}]. \tag{2}$$

Here $(d_{PM}^{2\omega})_{av}$ is an average taken only over phase-matchable components and θ_{PM} is the phase-matching angle measured from the crystal's optic axis. The constant of proportionality in Eqs. (1) and (2) is identical and involves primarily the refractive indices of the powder at the fundamental and second-harmonic frequencies.

Thus Eqs. (1) and (2) predict a significant difference in the second harmonic intensity for powdered materials according to the magnitude of their nonlinearity and their phase matchability, when measured under identical experimental conditions.

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The experimental arrangement is shown in the schematic of Fig. 1. The laser source was Nd:YAG operating at a wavelength of 1.06 μm. It was continuously pumped and repetitively Q-switched at 2 kHz, with an average output power of about 0.1 watt in an unpolarized 3-mm-diameter beam. Powdered samples were prepared by grinding small crystalline pieces and sorting with sieves to obtain particle sizes in the range 74 to 125 μm. The powder was placed in a 2-mm-thick cell with fused quartz windows and irradiated at normal incidence. Second-harmonic light at 0.53 μm was detected by an S-11 photomultiplier placed directly behind the cell. Appropriate glass and interference filters were used to isolate the harmonic radiation. The photomultiplier output was amplified and rectified in a phase-sensitive amplifier, and the resultant dc-level signal was displayed on a strip-chart recorder. A portion of the laser beam was monitored by a photodiode to provide a synchronizing signal for the phase-sensitive amplifier.

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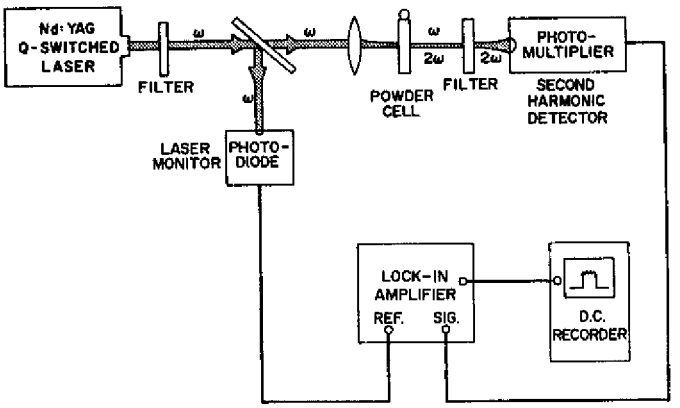

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The results of our powder measurements are presented in Table 1 for 21 crystalline materials. The ratio of second-harmonic intensity observed for each material relative to a powdered $LiIO_3$ standard is tabulated in the fourth column. The ratios of previously measured materials, which have been renormalized to $LiIO_3$ for ease of comparison, are shown in the fifth column. The sixth column indicates the method of preparation of the materials studied in this report.

Sixteen of the materials investigated were iodate compounds. Eight of these had not previously been measured either as single crystals or by the powder technique. They were $Mg(IO_3)_2 \cdot 4H_2O$, $Ca(IO_3)_2$, $Co(IO_3)_2$, $Cu(IO_3)_2$, $Cu(IO_3)_2 \cdot H_2O$, $Zn(IO_3)_2$, $AgIO_3$, and $Cd(IO_3)_2$ and are indicated by dashes in the fifth column. None of these new iodate compounds showed appreciable second-harmonic intensity, indicating low nonlinear coefficients or lack of sufficient birefringence for phase matching. $Co(IO_3)_2$, $Cu(IO_3)_2$, and $Cu(IO_3)_2 \cdot H_2O$ show absorption structure in the visible, and this may contribute in part to a reduction in their observed second-harmonic intensity.

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$NaIO_3$	mmm	White	0.004	0.000†	Same as above.
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$Zn(IO_3)_2$	—	White	0.017	—	Gel method using $ZnCl_2$ and HIO_3.
$RbIO_3$	mm2	White	1.2	2.7†	Slow evaporation of hot aqueous solution.
$AgIO_3$	—	White	0.033	—	Slow evaporation of NH_4OH solution.
$Cd(IO_3)_2$	—	White	0.042	—	Slow evaporation of hot NH_4OH solution.
$CsIO_3$	3m or 2	White	0.14	0.07†	Slow evaporation of hot aqueous solution.
$NH_4H_2PO_4$	$\bar{4}2m$	White	0.04	0.05†	Aqueous solution.
$Ba_2NaNb_5O_{15}$	mm2	White	2.6	2.6*, 6.7‡	Kyroupulos melt growth.
$C_{10}H_8O_3$	—	White	0.022	0.067‡	Slow evaporation from solutions of ethanol.
$C_9H_6O_2$	—	White	0.18	—	Slow evaporation from solutions of benzene and acetone.
$C_{14}H_{17}NO_2$	—	Yellow	0.4	0.6‡	Slow evaporation from solutions of benzene and acetone.

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1.06 μm and, as such, is a useful analytical tool to the nonlinear materials research program at NRL. Furthermore, an extension of this technique using a CO_2 laser at 10.6 μm should allow an initial evaluation of potential nonlinear materials for use in the infrared.

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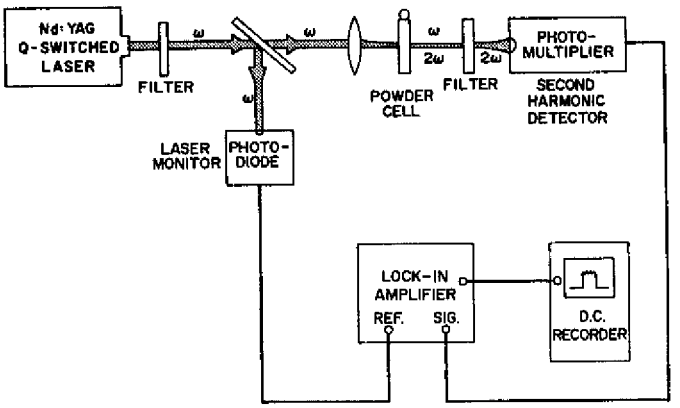

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